



# Mass-producible hydrophobic perfluoroalkoxy/nano-silver coatings by suspension flame spraying for antifouling and drag reduction applications

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## ABSTRACT

To exploit marine metal materials with antifouling and drag reduction properties, we constructed hydrophobic perfluoroalkoxy (PFA)/nano silver (Ag) coatings onto aluminum substrates by suspension flame spray deposition of PFA/AgNO<sub>3</sub> composites. Silver nanoparticles were formed in situ within PFA coating during the suspension flame spraying. The successful construction of PFA/nano-Ag coatings was revealed by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and contact angle measurements, respectively. The additional silver nanoparticles play the significant role in regulating the sliding angle of the PFA-based coatings. The silver nanoparticles-loaded hydrophobic PFA coatings synergistically inhibited the adhesion of bacteria, while only PFA coatings with lower content of silver display drag reduction property. The simple and cost-effective approach is of great promise in mass-production of antifoulant-loaded hydrophobic coatings on general substrates for potential antifouling and drag reduction applications.

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## 1. Introduction

Antifouling and low drag surfaces are two key issues of marine vehicles [1–3]. The settlement of marine fouling on the marine vehicles causes drag-related speed loss and increased fuel consumption [4–9]. During the past decades numerous research efforts have been devoted to investigating mechanism and application technologies of antifouling and drag reduction [10–14]. However, only a few reports have been published on the combine effect of antifouling and drag reduction [3, 15].

Recently, hydrophobic surfaces have drawn much attention as a new route for antifouling and drag reduction. For instance, the antifouling and drag reduction of hydrophobic surfaces in seawater was reviewed by Ferrari et al. [16]. The rice leaf and butterfly wing effect have been reported to develop novel hydrophobic surfaces for antifouling and drag reduction applications, as reviewed by Bixler et al. [17]. Many processing techniques have been attempted to fabricate hydrophobic surfaces [18]. However, most of these strategies still have difficulty in mass-production of hydrophobic surfaces. To overcome the aforementioned

limitations of bioinspired hydrophobic surfaces, previously, we successfully fabricated hydrophobic coatings by suspension thermal spray [19, 20]. This approach can be used to fabricate hydrophobic coatings on general substrates with arbitrary shapes and sizes. To the best of our knowledge, there is no report describing the suspension thermal sprayed hydrophobic coatings for antifouling and drag reduction simultaneously.

Except for hydrophobic surfaces, the incorporation of antifoulant was also proved to be an efficient approach to impose antifouling property on marine surfaces [21], leading to low drag surfaces. It is well known that heavy metals, such as copper and silver, have strong antifouling effect towards a broad range of marine fouling. The antifouling mechanism of heavy metals was believed that metals ions adhered to the cell walls of marine fouling organisms, causing disruption of the permeability and organism death [22].

We hypothesized that hydrophobic coatings with antifoulant-loaded could inhibit the adhesion of biofouling and possess good drag reduction properties simultaneously. To confirm the hypothesis, aluminum substrates with polyfluoroalkoxy (PFA) coating and silver-loaded PFA coating were fabricated by suspension flame spraying and the synergistic effect of hydrophobicity and antifoulant of the PFA-based composite coatings on the regulation of antifouling and drag reduction properties were investigated.

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## 2. Experimental part

Aluminum plates (20 mm × 25 mm × 2.5 mm and 200 mm × 300 mm × 11.2 mm) were employed as substrates. Polyfluoroalkoxy with the size range of +30–100 μm (PFA, Shenzhen Taotao Suhua Co. Ltd., China) was used for facilitating the hydrophobicity. PFA-based coatings were deposited by suspension flame spray (Wuhan Research Institute of Materials Protection, China) [19]. In this study, silver was chosen as a typical antifoulant, due to its strong antibacterial effect [23–25]. For PFA-based suspension preparation, PFA powder with a concentration of 5.0 wt% was added into ethanol solution and the suspension with silver nitrate (AgNO<sub>3</sub>, Aladdin Chemistry Co. Ltd., China) concentration of 0 wt%, 1.0 wt% and 10.0 wt% were explored, respectively. The as-sprayed coatings were designated as PFA coating, PFA/1%Ag coating and PFA/10%Ag coating, respectively.

Field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands) was used for microstructure characterization of the coatings. Phases of the samples were evaluated by X-ray diffraction (XRD, Bruker AXS, Germany). Chemical composition of the samples was examined using Fourier transform infrared spectroscopy (FTIR, model 6300, Bio-Rad Co. Ltd., USA). Water static contact angle (CA) and sliding angle (SA) measurements were characterized using a video-based optical system (Dataphysics OCA20, Germany) by measuring five points for each sample. The water droplet size was 5 μL for CA measurement and 15 μL for SA measurement.

To investigate the release behavior of silver ions from the silver nanoparticles-loaded PFA coatings, PFA/1%Ag coating and PFA/10%Ag coating were immersed into a 6-well plate containing 7 mL sodium chloride (NaCl) solution in each well at room temperature for 7 and

21 days. The cumulative release of silver was monitored using an inductively coupled plasma optical emission spectrometer (ICP-OES, PE Optima 2100DV, Perkin-Elmer, USA).

Gram-negative *Escherichia coli* (*E. coli*), which was extensively studied for marine environment [26–33], were employed as the simplified model to evaluate the antifouling property of the samples in this study. *E. coli* were cultured in LB media (1.0% of NaCl, 0.5% of yeast extract and 1.0% of tryptone) shaken at 37 °C for 24 h. The *E. coli* suspension with an initial concentration of 10<sup>6</sup> cells/mL was prepared in artificial seawater (ASW). The samples were washed with ASW for three times after incubated for 24 h. For FESEM observation, the samples were fixed by 2.5% glutaraldehyde for 2 h and dehydrated by critical point drying using a graded series of ethanol.

Drag reduction tests were performed in cavitation tunnel system (China Ship Scientific Research Center, China). The flow velocity in test section is adjustable between 0 and 25 m/s. The flow velocities with 5, 8 and 11 m/s were chosen in this study. To comparatively investigate the influence of the coatings on drag, aluminum substrates, PFA coatings, PFA/1%Ag coatings and PFA/10%Ag coatings were systematically performed. Drag coefficients ( $C_f$ ) were calculated according to the equation:

$$C_f = \frac{Z}{0.5\rho V^2 A}$$

where  $Z$  is the resistance of the samples;  $\rho$  is the density of water;  $V$  is the flow velocity in test section; and  $A$  is the projected area of the samples. Each measurement was performed for three times. Drag reduction

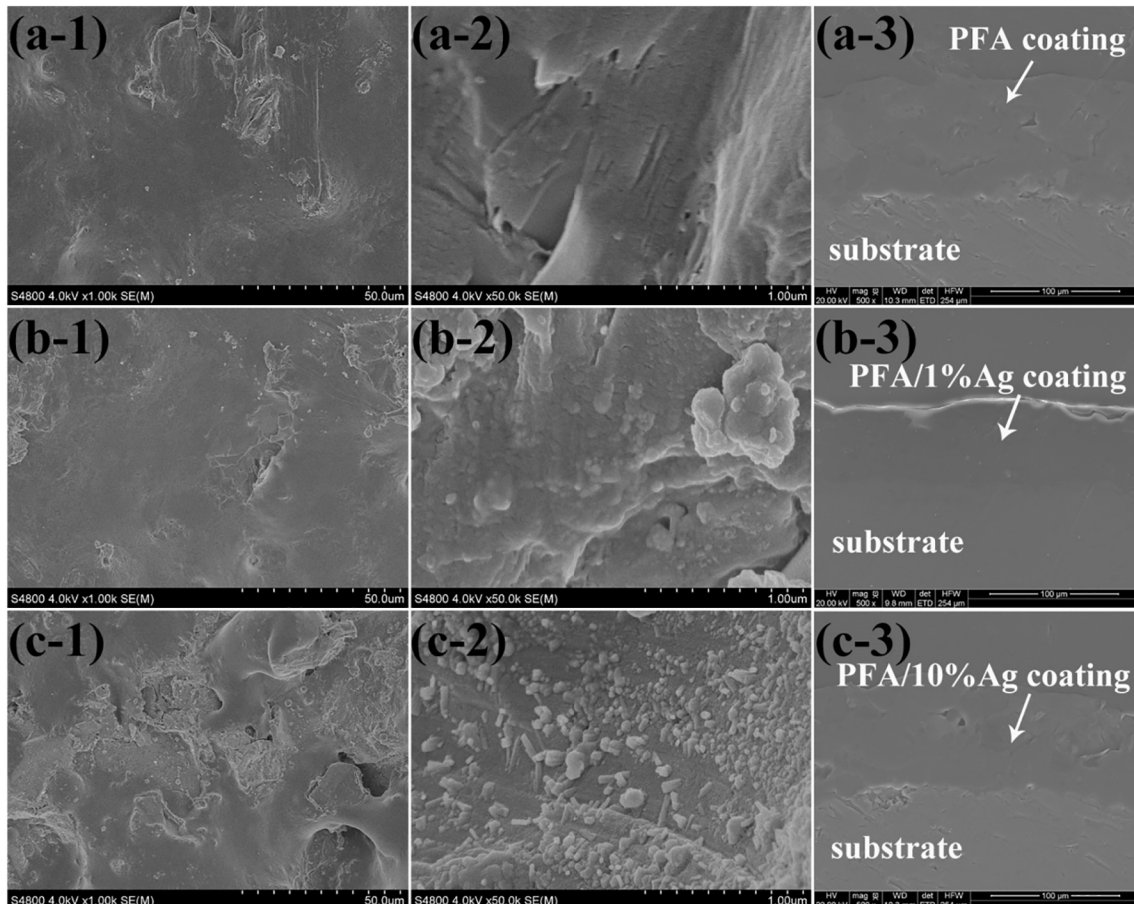


Fig. 1. FE-SEM images of (a) the PFA coating, (b) the PFA/1%Ag coating, and (c) the PFA/10%Ag coating. (-2 is enlarged view of selected area in -1, -3 is cross-sectional view of the coating).

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